POSSIBILITIES FOR PRODUCING NEW GLASSES IN SPACE

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ABSTRACT

In July, 1968, Mr. Hans Wuenscher of the NASA Marshall Space Flight Center visited the Space Division of the North American Rockwell Corporation and discussed the many possibilities for manufacturing in the "zero gravity"[1] environment of space. Zero gravity conditions of earth orbit have been known for a long time, but, until recently, very little serious thought had been given to the possibilities for exploiting these conditions for technical and, ultimately, commercial purposes.

Many of the concepts that emerged from a preliminary study were concerned with the potentially significant advantages attending the melting of materials in space free of gravitational restrictions. While such feats have been performed on a limited scale on earth

> Zero gravity melting permits the elimination of a solid container during both the melting and cooling phases of glass production. The combination of superheating well above the melting temperature and cooling in the absence of most normal nucleation sites promises to permit the production of glasses from normally crystalline materials such as Al_2O_3, HfO_2, ZrO_2, etc. Such glasses should find immediate applications in refractive optics, where the unusual combinations of index of refraction and dispersion can be used to advantage in highly corrected multi-element lenses. The possibilities for returning supercooled liquids as glasses from orbit and growing single crystals on earth is discussed. Heating equipment and atmospheres for space melting of glasses are considered.

[1] "Zero gravity" is used here to describe the condition of equillibrium between earth's gravitational pull and the centrifugal forces of earth orbit, or in other words, a condition of perpetual free fall.

("levitation melting" of metals supported by an induction field), here appears to be an opportunity to melt almost any material without the restrictions imposed by a container. No longer need "levitation melting" be limited to only 15 to 20 grams of materials with high electrical conductivity. In zero gravity almost any inorganic material can be melted without requiring a container if a suitable atmosphere and heat source can be provided. The surface tension forces cause the liquid material to assume a spherical shape. Melting in space, therefore, has been dubbed "containerless melting" to distinguish it from "levitation melting", which term can be reserved for processes performed in a normal gravitational field.

Initial efforts at space melting can be justified only where the resultant product cannot be made on earth with today's state-of-the-art. Such an approach necessarily takes us into relatively unknown and quite possibly controversial territory. A corollary requirement is that the ultimately resultant product be sufficiently useful to justify the expense of the initial experimental work.

The balance of this paper deals with one of the many possible concepts involving containerless melting--that of producing new (inorganic) glasses in space. For purposes of this discussion, the definition of glass given in Shand (Reference 1) is appropriate--"An inorganic product of fusion which has been cooled to a rigid condition without crystallization." Most of the emphasis in the study to date has been on the possibilities for new glasses composed of metal oxides. Less emphasis has been placed on chalcogens. There are, no doubt, possibilities for producing glasses of other types of compounds, such as halides and nitrides, or for that matter, of metals, but time has permitted only superficial consideration of them to date.

To appreciate the possibilities for producing new glasses in space, it is necessary to explore further some of the really unique aspects of zero gravity melting. Not only is it theoretically possible to melt very high melting point substances without contamination from container materials but, of equal importance for the production of glass, it is also possible to cool the substance free of any contact with solid material. Thus many of the usual sites for nucleation of crystals can be eliminated. Is it possible that elimination of the easier nucleation sites could result in complete suppression of nucleation, and therefore of crystallization, of materials such as Al_2O_3, TiO_2, etc? This is a question that will be dealt with, if not fully answered, in more detail later. Another question that will be explored is--assuming glasses could be made from materials normally obtainable only in the crystalline state--would they be useful technologically?

Another appealing feature of the concept of glass-making in space is the relative simplicity of the operation, resulting in a spherical boule of optical glass. Such a shape is quite useful for the production of lens elements. The techniques for cutting, shaping, and figuring lens blanks into the final configuration are well known and need not be elaborated on further here. It is conceivable then that, given a well-engineered facility and a modest amount of special training, an astronaut can perform the necessary space operations. The more technically complex operations of selecting, refining, and preparing the starting materials and the highly skilled post-flight operations of property measurements, lens grinding, figuring, coating, etc., could be performed on earth with conventional techniques.

Assuming that unusual glasses can be made in a zero gravity environment, there are possibilities that single crystals might be grown from the glass boules after returning them from space.

GLASS APPLICATIONS

VISIBLE TRANSMITTERS

Most of the optical glasses used for refractive optics in the visible region of the spectrum are based on the dioxide of silicon, SiO_2. The large range of optical properties required for sophisticated, multi-element lenses are achieved commercially by incorporating other oxides, such as PbO, La_2O_3, Al_2O_3, CaO, etc., with the SiO_2 base. There are two other glass formers, B_2O_3 and P_2O_5, that in recent years have been employed as bases for the specialized optical glasses required for today's better optical devices. These three base oxides, SiO_2, B_2O_3, and P_2O_5, are all very viscous in the molten state, a property that reduces mobility sufficiently to prevent nucleation and crystallization on cooling so that a glass results. A glass, then, might be considered a supercooled liquid with very high viscosity. As such it is amorphous, or without the long range, repeatable structure found in the solid, crystalline state. While recent studies have shed much light on the nature of the "structure" of glass and have shown that it bears some resemblance to the crystalline state, the differences are of great significance in terms of the unique properties[1] that make glasses useful in refractive optical applications.

The principal characteristics of glasses that make them useful in refractive optical applications are:

1. Transparency
2. Hardness
3. Chemical durability
4. Index of refraction (n)
5. Dispersion ($dn/d\lambda$)
6. Optically isotropic

[1]For a more complete dissertation on the essential features of glass, the reader is referred to a clearly written artical by Dietz (Reference 2).

The last three characteristics are of prime importance in multi-element lenses. Since many crystalling materials are normally anisotropic and hence have more than one index of refraction, they are unsuitable for refractive optical applications. If, however these materials can be produced optically isotropic, they then become potentially useful for refractive optical applications. For example, crystalline SiO_2 is anisotropic, while glasses formed from SiO_2 are isotropic. In other words, the number of materials useful for refractive optics applications would be increased significantly if normally anisotropic materials can be produced with isotropic optical properties.

TABLE 1 lists some pertinent optical properties, taken from the published literature, in the visible range of the spectrum for a number of transparent oxides. The structure for which the data applies, where known, is noted. For those crystalline substances which are anisotropic and uniaxial, the data for both the ordinary ray (ω) and extraordinary ray (ϵ) are given. Of those substances listed only monoclinic ZrO_2 and HfO_2 are biaxial -- therefore three indices and dispersions are given. The data listed include the index of refraction at the sodium D (yellow) line and the inverse rate of change of index with wavelength. This latter property, given by the Abbe number, ν_D, is a function of the refractive indices of the blue hydrogen F line, yellow sodium D line, and red hydrogen C line (n_F, n_D, and n_C) and is given by the relationship $\nu_D = \frac{n_D - 1}{n_F - n_C}$

It should be borne in mind that the Abbe number is in inverse relationship to the dispersion -- low dispersion glasses having high Abbe numbers and vice versa. The index of refraction for all materials characteristically decreases with longer wavelength as is shown schematically in FIGURE 1. Low dispersion materials have flatter and high dispersion, steeper curves.

The data from TABLE 1 are plotted in FIGURE 2, the traditional $n - \nu$ diagram used in the optical glass industry. It should be noted that the data points for the anisotropic crystalline materials are the mean values as calculated by the formulas:

$$\text{mean} = \frac{2\omega + \epsilon}{3} \quad \text{or} \quad \frac{\alpha + \beta + \gamma}{3}$$

where $\omega, \epsilon, \alpha, \beta, \gamma$ stand for the ordinary and extraordinary ray of uniaxial crystals and the three rays of biaxial crystals, respectively.

The area shown in FIGURE 2 encloses the n, ν values for virtually all of the commercially available optical glasses. The development effort over the past 100 years or so has concentrated on filling

in the areas between the low index, low dispersion crown glasses and the higher index, high dispersion flint glasses. In recent years the trend has been to expand the available glasses in the higher index, lower dispersion direction. One of the present goals of some optical glass producers is to achieve the properties of spinel ($MgAl_2O_4$).

If it becomes possible to obtain some of the oxides shown as glasses by melting and cooling in zero gravity, a major expansion of optical glass properties could be achieved. Of particular interest are the oxides of aluminum and hafnium, both of which combine unusually low dispersions with high index of refraction.

It should be emphasized that we are talking about only the pure oxides which might be used as bases for new glasses. If the pure oxides could be obtained as glasses, it is logical to assume that mixtures could be produced to fill in the area needed on the n - ν curve to supply the optical designer with the selection of properties needed to create new, highly corrected lenses.

In recent years there has been increasing emphasis on producing highly corrected lenses of increasingly high aperture. In such lenses an error known as secondary spectrum becomes significant. The secondary spectrum can be defined as the residual chromatic aberration that remains after two wavelengths have been brought to a common focus using conventional achromizing techniques, and is determined by the partial dispersion ratios[1] of the optical materials used in the system.

In order to appreciate more fully the potentials for new glasses if they could be made in space, it is necessary to consider the role of partial dispersion. As the relationship $L = f\left(\frac{P_a - P_b}{\nu_a - \nu_b}\right)$ shows for a two-component achromat, the secondary spectrum (L) is a function of the focal length (f), the partial dispersion ratios of components a and b (P_a and P_b) and the Abbe numbers of the components. In order to minimize L the numerator should be small and the denominator large. Unfortunately, nature has apparently decreed that the P, ν points for glasses of a given base all fall on a single line, for example lines SS, BB, and PP of FIGURE 3.

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[1]The partial dispersion is essentially the ratio of the slope of a portion of the n vs. λ curve to that of a larger portion. A ratio sometimes used is $P_{FD} = \frac{n_F - n_D}{n_F - n_C}$ For a more complete discussion of the role of partial dispersion in the correction of secondary spectrum and the relationships to optical glasses. the reader is referred to a paper by Brewster, Hensler, Rood, and Weidel (Reference 10).

In order to correct secondary spectrum, it is necessary, then to choose glasses of more than one base for the individual elements of the lens. This consideration has prompted a leading producer of optical glasses and optical equipment to develop the non-cross-bred[1] borate and phosphate glasses to provide a useful range of Abbe numbers. The secondary spectrum correction possibilities are limited with conventional glasses, however, because the horizontal displacement of the three lines of FIGURE 3 is quite small.

Undoubtedly, if new bases for optical glasses could be found, new families of glasses with different P - ν lines could be created and the possibilities for secondary spectrum correction thereby significantly increased. Unfortunately, it is not possible to predict the location of the lines for such glasses at this time. Partial dispersion calculations require that the index of refraction be known to five or six significant figures. Even if data of such accuracy were available for the crystalline materials being considered in this report, the imprecise conversion of data from the crystalline to the glassy condition would render the exercise meaningless.

INFRARED TRANSMITTERS

In recent years the advancement of infrared technology has delineated requirements for materials which are transparent in the infrared portion of the spectrum. Good infrared transmission is, by and large, characteristic of many semiconductor materials, i.e., silicon and germanium amoung the elements and the chalcogenides among the compounds. The infrared transmitting chalcogenides[2] are composed of group IV-A and V-A elements, with sulfur, selenium, and tellurium of group VI-A.[3] Among the two-component chalcogens, the compound, As_2S_3, is a strong glass former. By rapid quenching from the molten state, glasses can be formed from certain As-Se, Ge-S, and Ge-Se compositions and a number of ternary and quaternary compositions. Unfortunately, the chalcogenide glasses obtained to date are soft

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[1] i.e., borates free of silicates and phosphates, etc.

[2] For a good discussion of the state-of-the-art of infrared transmitting glasses, the reader is referred to articles by A. Ray Hilton, and A. J. Worrall (References 11, 12).

[3] Oxygen, also in group VI-A, causes infrared absorption in the sulfide, selenide, and telluride glasses. Therefore strong efforts are made to exclude it.

and have low softening temperatures. Zero gravity melting and cooling may make it possible to obtain glasses with improved hardness and higher softening temperature from compositions with higher Si and/or Ge contents, or possibly even containing elements from groups other than IV-A and V-A.

Silicon and germanium have superior mechanical properties but are not suitable for infrared transmission at higher temperatures because of significant "holes" in the transmission spectrum. If they could be obtained as glasses, there is the possibility that the holes might disappear, rendering them among the most promising candidate materials for infrared transmitting applications. It appears that the chances for successfully melting and cooling any metal to a glass in space are significantly smaller than that for compounds, however.

GLASS MAKING FEASIBILITY

The discussion in the previous section was based upon the assumption that new glasses can be made in zero gravity. This section examines that assumption in terms of the possibilities for suppressing nucleation of crystals, atmospheres that might be used, and possible heating methods.

NUCLEATION AND CRYSTALLIZATION

Work by Duwez (Reference 13) and others demonstrate that crystallization can be suppressed in tellurium and some metal-based systems through the use of extremely high cooling rates from the liquid state. By using thermal conductance to obtain cooling rates on the order of 10^6 C per second, glasses have been formed from tellurium-based systems with low melting eutectic additions of Ga, In, Ge, Cu, and Cu-Au. Among the metal-based systems studied by Duwez and others, the low melting eutectic compositions of the systems Fe-P-C; Au-Si and -Si-Ge; Pd-Si, -Si-Fe, -Co, -Ni, -Ge; Pt-Si, -Ge, -Sb; and Rh-Ge have been obtained as glasses on a laboratory scale. It appears unlikely that the methods used to rapidly cool are capable of suppressing nucleation entirely, but they obviously are effective in preventing crystal growth, which is a time-dependent phenomenon. The main point here is that it has been shown to be possible to prevent detectable crystallization even in metal systems, with their very high heats of fusion and very low viscosity.

Are the conditions present in zero gravity melting and cooling, then, sufficient to prevent crystallization in oxides? While the cooling rates obtainable under the conditions anticipated in space, being dependent solely on radiation losses, are rapid, at least for the higher melting materials, they cannot approach the rates obtainable by conduction cooling of metals in the laboratory. Therefore, the basis for predicting that zero gravity melting and cooling can result in unusual glass formation appears to rest strongly on the possibilities for suppressing nucleation, at least for the first 600 degrees or so of cooling below the normal freezing point.

Assuming that all residual nuclei from the crystal state can be destroyed in the molten state, possibly by heating to 10 or 20 percent above the melting point, will the materials spontaneously

nucleate? This is a question that cannot be resolved without further study. It is possible that there may be no such thing as truly spontaneous nucleation in glasses. Ernsberger and Neely have pointed out that nucleation does not occur preferentially at bubble surfaces in plate glass (Reference 14) as was originally thought by many to be the case. Ernsberger (Reference 15) has also pointed out that invariably, in cases where spontaneous nucleation was thought to occur during devitrification of silicate glasses, closer examination has revealed other explanations. In one case, small pieces of undissolved platinum from the melting crucible were present in each crystallite examined. The platinum undoubtedly served as a nucleation site. In other instances evidence for "spontaneous" nucleation have been explained on the basis of chemical changes at the outer surfaces of a glass body or at crack surfaces. The "spontaneous" nucleation that apparently occurs in crystallized glasses, such as Cer-vit and Pyroceram, can be explained on the basis of a two-stage process involving separation into two liquid phases. Liquid-liquid nucleation is known to have a lower energy barrier than liquid-solid nucleation.

At any rate, it is anticipated that nucleation (and therefore crystallization) in zero gravity can be suppressed for the following reasons:

1. Oxides are excellent solvents for expected impurities. Therefore, the chances are very good that impurities that could serve as nucleators can be completely dissolved. The elimination of a solid container precludes the possibility of contamination from that source.

2. Because materials being considered can be superheated without contamination from a crucible, it appears possible that all of the residual nuclei from the crystalline starting material can be destroyed.

3. The cooling rates obtainable by radiation, especially for the higher melting temperature materials, can be very high. Since the materials are transparent, radiation can occur from within the bulk of the material as well as from the surface. Cooling rates therefore should be quite uniform. This should also reduce the tendency to fracture on cooling, even if the glasses formed have relatively high thermal expansion coefficients. Radiation cooling rates will be highest at the higher temperatures where rapid cooling is most important if nucleation is to be suppressed. If a sufficient amount of supercooling can be achieved, increasing viscosity should prevent nucleation and crystal formation at the lower temperatures, where cooling rates will decrease.

4. Many of the oxides being considered at this time have a tendency to be glass formers in spite of their never having been observed in the amorphous condition in the massive, pure form. It is the writer's understanding that Al_2O_3, for example, can be treated as a glass former in silicate glass research (Reference 16). Al_2O_3 base glasses free of SiO_2 , B_2O_3, or P_2O_5 are being produced commercially (for example, CaO-BaO-MgO-Al_2O_3) (Reference 12). Recent work in the Soviet Union has shown that there is a large glass forming area in the ternary system, TeO_2-V_2O_5-BaO, which extends into the three binary systems (Reference 17). None of the three pure oxides are glass formers under normal circumstances. In these instances, for example, zero gravity processing may provide the means for preserving the amorphous form on cooling even in the pure oxides. If this can be done, glasses can be formulated on the basis of obtaining desired optical properties without the restrictive necessity of choosing compositions with low mobility.

In summary, it is not possible to state with finality at this time that zero gravity processing will prevent nucleation per se. It does appear reasonable, however, that the combination of circumstances attending melting and cooling in zero gravity will permit the production of glasses from substances never before observed in other than the crystalline form.

ATMOSPHERES, EVAPORATION, AND DECOMPOSITION

While high vacuum and virtually infinite pumping capacity are available for the taking in space, it does not appear obvious that the high vacuum can be used to advantage for melting the materials being considered here. Several considerations appear to counter-indicate its use:

1. Evaporation and decomposition of the compounds being considered would be accelerated in a vacuum.

2. The transfer of condensible materials from the melt to cooler surfaces might be particularly troublesome in space.

3. There is a possibility that bubbles might form within the melt, being generated by outgassing products such as oxygen, metal, and oxide vapor. If this happens, the lack of gravity may prove to be a disadvantage. In the absence of gravity there can be no buoyancy effect--the principal means by which bubbles are removed from melts in conventional earth melting processes.

The most reliable information located to date on the melting and "boiling" points of some of the oxides being considered are listed in TABLE II. For comparison purposes, data for the three conventional glass formers are given at the bottom of the table. The melting and boiling points for MgO and SrO are quite close together at atmospheric pressure. For example, if one were to assume that MgO does not decompose on vaporizing, the Langmuir equation[1] can be used to calculate the evaporation rate. On this basis the evaporation rate for MgO at pressures less than about 10^{-5} torr is calculated at about 3000 cm/hr. at its melting point (2825C). In other words, a 10cm. diameter sphere of molten MgO, if suddenly subjected to the vacuum of space, would completely disappear by evaporation in about 6 seconds. Similar calculations for Al_2O_3, ZrO_2, and TiO_2 yield evaporation rates less than 1 cm./hr.[1] Such rates would not pose a serious problem in terms of material loss, but could be serious in terms of material transfer by evaporation and condensation. For example, the reflective surface of a solar furnace could become rapidly coated, or windows used for observation of the melting process in chambers could rapidly become clouded.

It must be emphasized at this point that the basic assumption leading to the calculations cited above is not, strictly speaking, a valid one. A cursory survey of the literature indicates that most of the oxides in TABLE II vaporize incongruently. Al_2O_3, HfO_2, La_2O_3, TiO_2, and SiO_2 all decompose to their constituent elements and/or to suboxides at the temperatures required for melting (References 18, 19, 22, 23, 24, 25) depending upon the ambient atmospheric composition and pressure. For example SiO_2 in vacuum at 2000 K will vaporize as Si, SiO, O, and O_2 at a total pressure of about 10^{-3} atmospheres, whereas in the presence of O_2 at 1 atmosphere the escaping species will be predominantly Si, SiO_2, and O_2 at a total pressure of about 10^{-6} atmospheres. The ambient atmosphere will have a much smaller influence on oxides which tend to vaproize congruently. For example, BeO tends to form polymeric vapor species as $(BeO)_n$, where n = 2,3,4,5,6. In this case even a very small partial pressure of O_2 will suppress incongruent vaporization.

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[1]The Langmuir equation was used in the form: $R = \frac{Kp}{d\sqrt{T/M}}$

where
R=rate of evaporation, cm./hr.
K=2.1 x 10^2
d=density, gm./cc.
T=temperature, ^oK
M=molecular weight
p=vapor pressure, mm. of Hg

For these calculations the vapor pressure at the melting point was assumed as:
4 x 10^2 for MgO
5 x 10^{-3} for Al_2O_3
1 x 10^{-1} for ZrO_2
6 x 10^{-3} for TiO_2

Another type of vaporization can occur if solids of varying stoichiometry may form, as for example, TiO_2. Careful control of oxygen pressures may prove essential in these cases.

It would appear that an oxygen atmosphere would be preferable to a vacuum for melting most of the oxides. Suitable pressures can be calculated for those oxides where reliable thermodynamic data are available. This has not been done to date, nor has any serious thought been given to compounds other than oxides.

Regarding consideration 3 listed earlier, it should not be assumed, without further study, that bubbles will indeed form during high vacuum space melting. There is a strong possibility that, at least for the gasses that evolve at lower pressures, the pressure of evaporation or decomposition will be found to be less than the internal pressure of the melt. If such turns out to be the case, the mechanism for evaporation might consist of diffusion to the surface of the melt, and evaporation from the surface. In that event, bubble formation would not occur. It should be possible to pretreat the starting material by vacuum heating to eliminate the more volatile gasses while the bulk of the material is solid. This should leave only those gas formers whose pressures are less than the internal pressure of the melt. In any event, the internal pressure in the melt can be raised by increasing the atmospheric pressure surrounding the melt, a condition readily accomplished in a chamber.

HEAT SOURCES

In the present study a number of possible heat sources for melting the materials of interest have been considered:

1. Chemical reactions
2. Plasma
3. Electron beam
4. Induction
5. The sun (solar furnace)

One of the more obvious problems that must be handled in the design of equipment for space melting is the propulsion effect. Such an effect is present in varying degrees in the first three heating methods. Perhaps this effect could be turned to advantage by simultaneously directing four torches, electron beams, etc., at the melt. This could be arranged by aiming the "torches" at the melt

from directions normal to the faces of an imaginary equilateral triangular pyramid (the melt being in the center of the pyramid). Special consideration would have to be given also to removal of the products of combustion in the case of the first two methods.

The first four methods above all share a significant drawback for space melting of large sized heats. The power requirements should exceed anything attempted in space to date by a significantly large margin. This naturally leads to the last heat source listed above, the sun. It would appear logical to directly utilize in space the unlimited energy available from the sun. The maximum temperature available by solar heating, approximately 5700 K[1], is more than ample for any of the materials of interest.

An example of solar furnace that might be utilized in space is pictured in FIGURE 4. The furnace shown is conceived as essentially an unmanned spacecraft incorporating a sun sensor which keeps the optical axis pointing toward the sun. Also incorporated are three detectors, which serve to keep the focus of the parabolic mirror centered on the melt (small sphere near the furnace). All sensors are servoed electronically to attitude control jets located on the periphery of the furnace. The antenna shown permits manual override of the automatic functions by personnel in the orbiting workshop (upper right background). Such a design should permit the furnace to "chase" the melt as it moves with respect to the orbiting workshop. By incorporating a radiation pyrometer, possibly as one of the melt sensors, it should be possible to automatically hold a pre-set temperature by focusing and defocusing with respect to the melt. The flat ring around the parabolic reflector holds solar cells used to provide secondary power. Not shown in the rendition is a pressure vessel with a suitable window for permitting entry of solar energy. Such a vessel could be attached to the solar furnace and would contain the melting atmosphere. It could be sized to permit reasonable movements of the melt without contact with the vessel walls.

Large parabolic mirrors of suitable quality for the purpose can be made by the spin-casting process. The orbit of the workshop, of course, would have to be chosen to provide sufficiently long duty cycles in the sun. Such high inclination orbits should not be a serious problem for missions whose prime purpose is melting of materials.

Perhaps induction furnaces are more appropriate for initial, small scale flight experiments where suitable orbits may not be chosen because of conflicts with other experiments and because of a desire to keep astronaut extravehicular activity to a minimum.

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[1]The apparent black body temperature of the sun.

A discussion of induction units for space melting of metals has been presented by Frost (Reference 26). Induction heating appears possible for the materials being considered, most of which are poor conductors at ordinary temperatures. The effect of temperature on the electrical resistivity of a number of oxides is shown in FIGURE 5. The curve for graphite, a known good susceptor, is shown for comparison purposes. It is also known that zirconium dioxide is a satisfactory susceptor, with resistivity values in the 10^{-1} to 10 ohm-cm range. With the possible exception of alumina and magnesia, all of the oxides shown fall into this range or below it at temperatures well below their melting points. It is therefore apparent that most of the oxides shown could be induction heated without a susceptor provided they were preheated, perhaps in a resistance furnace. In the event AL_2O_3, and MgO are found to be too high in resistivity to permit induction melting, it might be possible to dope them with small additions of other materials to lower their resistivity without seriously affecting their optical properties as glasses.

In FIGURE 6 are shown several possible schematic arrangements for a space induction melting concept which might be suitable for initial flight experiments on a small scale. FIGURES 6A, B, and C show different methods for transferring the material from the preheating furnace to the induction field, and after cooling, to the retrieval device. In FIGURE 6C the preheating furnace, induction furnace, and retrieval device are all fixed with respect to the chamber. The different locations of the melt are accomplished by shifting the chamber on a track to different positions which register with the desired positions with respect to the melt. In an alternate arrangement (not shown) the preheating furnace, induction furnace, and retrieval mechanism might all be attached to a track within the chamber and moved by a remote control mechamism.

As Frost (Reference 26) has pointed out, a centering force will be required to maintain the position of the melt while the workshop shifts with respect to the melt position, due to astronaut motions and orbit eccentricities. It appears likely that the small forces required could be provided by suitably utilizing the forces of the induction field. By the same token the arrangement suggested for the "nozzles" in the chemical, plasma, and electron beam concepts could provide the restorative force necessary.

CRYSTALLIZATION OF SPACE GLASSES

If we presume that experiments to produce supercooled glasses are successful, then another prospect of material production becomes evident. This additional prospect is that of producing single crystals of material either than cannot be produced otherwise or that would have improved physical properties. The proposed procedure would seem to have its principal merit with those materials that are polymorphic or those that are incongruently melting, for the reasons to be described later.

Suppose we consider the glasses that might be produced in a space station. The special feature of glass production in space is the lack of a crucible for containing a molten mass. In the absence of contact with any other solid material, the prospects for heterogeneous nucleation are eliminated, so that (it is theorized) it will be possible to produce substantial supercooling in materials that readily crystallize when heterogeneous nucleation is not avoided. Presuming that the supercooled material has been brought to a temperature low enough to prevent devitrification, we can now contemplate the prospect of controlled crystallization from a single point in the glass body.

An apparatus for accomplishing this is shown in Figure 7. The glass body is more or less balanced on the point of a seed crystal, with further balancing provided by air jets (air bearings). The air jets are to be precisely adjustable so that they can come very close to the surface of the glass but are kept out of actual contact by air pumped through the jet tips. Now, whereas the glass body requires the special provision of zero-G environment, the crystallization experiment takes advantage of terrestrial gravitational field in order to maintain a firm contact between the glass body and the seed crystal.

The phenomenon we wish to promote is that of controlled crystallization of the glass body, with crystallization initiating at the seed contact, and progressing slowly through the glass body. It probably will be necessary to maintain the system at an elevated temperature in order to permit crystallization to progress at acceptable rates.

A potentially troublesome aspect of the proposed procedure can arise from release of heat during crystallization. If the heat generated cannot be conducted away from the crystallizing front rapidly, both temperature and crystallization velocity will increase with

time, and this may lead to uncontrolled heating and crystallization. Experience certainly has demonstrated that material supercooled some few tens of degrees below the normal freezing temperature will crystallize very rapidly with a flash of luminescence when a seed is introduced. At much lower temperatures crystallization kinetics will be much slower, and presumably at some appropriate temperature crystallization rates will be controllable.

In a number of materials, certain physical properties prevent their being prepared in single crystal form. For example, ZrO_2 melts at a very high temperature, which makes it impractical to produce ZrO_2 by normal Czochralski techniques. Furthermore, ZrO_2 suffers a destructive phase change at 1100-1200°C. If ZrO_2 could be produced as a glass in an orbiting laboratory, we could contemplate conversion of the glass to crystalline form at a temperature below 1100°C, and thereby avoid the polymorphic transition. Beryllium oxide also suffers a polymorphic transition about 500°C below the melting temperature. There would be a real advantage, therefore, to be able to crystallize BeO from a glass body at a temperature below the transition temperature.

This crystallization process may be of value also in the formation of crystals whose composition melts incongruently. An example of this is beryllium silicate ($2BeO{:}SiO_2$, phenacite) whose decomposition point is about 1550°C. Crystals of this composition, therefore, are not amenable to being produced by Czochralski techniques. However, by crystallization from glass of the same composition, it may be feasible to prepare large crystals of compounds that exhibit incongruent melting. Another example is zircon ($ZrO_2{:}SiO_2$).

Throughout this discussion, no attempt has been made to identify materials that would have special economic or technological value. Such identification necessarily will require a more thorough investigation than has been done to date. The discussion, however, does point out some possible materials processes that potentially can expand the value of new glasses made in space.

CONCLUSIONS

Tentative conclusions based on the study conducted to date are:

1. There is a strong possibility that oxides such as Al_2O_3, ZrO_2, HfO_2, TiO_2, and others might be obtainable as glasses through space melting and cooling.

2. Glasses produced from such oxide bases would have optical properties not obtainable in the conventional silicate, borate, and phosphate-based glasses.

3. The combination of optical properties obtainable in such glasses should make them suitable for use in advanced optical systems, especially high resolution multi-element lens systems.

4. The spherical shape of glass boules that would result naturally from space production is quite suitable for the making of lenses and windows.

5. The production of glass, given a well-engineering space facility, should be well within the capabilities of astronauts after a suitable training period.

6. It may be possible to grow single crystals from glasses of suitable composition.

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R. Hensler of Bausch and Lomb, Inc. of Rochester, New York
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Table 1. Optical Properties of Some Oxides

Oxide	Structure	Ray	n_D	ν_D (calculated)	Source of Data
Al_2O_3	Rhombohedral (corundum)	ω ϵ	1.7686 1.7604	71.8 73.1	(Reference 3) (Reference 3)
CeO_2	Cubic (film, polycryst)		2.148	8-10	(Reference 4)
HfO_2	Monoclinic	α β, γ	2.070 2.146	37 44	(Reference 5) (Reference 5)
$MgAl_2O_4$	Cubic		1.72	63	(Reference 6)
MgO	Cubic		1.73790	54.3	(Reference 7)
Nb_2O_5	Unknown (film data)		2.258	8	(Reference 8)
Ta_2O_5	Unknown (film data)		2.091	23	(Reference 8)
TiO_2	Tetragonal (rutile)	ω ϵ	2.6124 2.8993	10.5 9.3	(Reference 3) (Reference 3)
	Unknown (film data)		2.657	9	(Reference 8)
ZnO	Hexagonal (zincite)	ω ϵ	2.013 2.029	15.8 14.9	(Reference 3)
ZrO_2	Monoclinic	α β γ	2.13 2.19 2.20	~5	(Reference 9)

Table II. Melting and "Boiling Points" of Some Oxides

Oxide	Melting Point, °C(T_m)	Boiling Point, °C(T_b)	Source of Information***** T_m	T_b
Al_2O_3	2050	2980	(18)	
BeO	2547	3787*	(18)	(18)
HfO_2	2897	~5400	(19)	
La_2O_3	2207	~2590**	(19)	(19)
MgO	2825	3260***		(18)
Nb_2O_5	1485-1512		(20, 21)	
SrO	2430	~3000		
Ta_2O_5	1875		(20, 21)	
TiO_2	1870	2500-3000	(18)	
ZnO	>1800	Subl. 1800		
ZrO_2	2675	4275****	(18)	(18)
SiO_2	1610	3273	(18)	(18)
B_2O_3	450	1500		
P_2O_5	570	Subl. 300		

*Listed T_b is temperature at which some of partial pressures of species in the vapor = 1 atm
**By extrapolation of the vapor pressure vs. temperature curve for the reaction, $La_2O_3 \rightarrow LaO+O_2$
***Temperature at which $\Delta F \rightleftharpoons O$ for $MgO(\ell) = MgO(g)$
****Temperature at which $\Delta F \rightleftharpoons O$ for $ZrO_2(\ell) = ZrO_2(g)$
*****References not listed are from The Handbook of Chemistry and Physics, various editions.

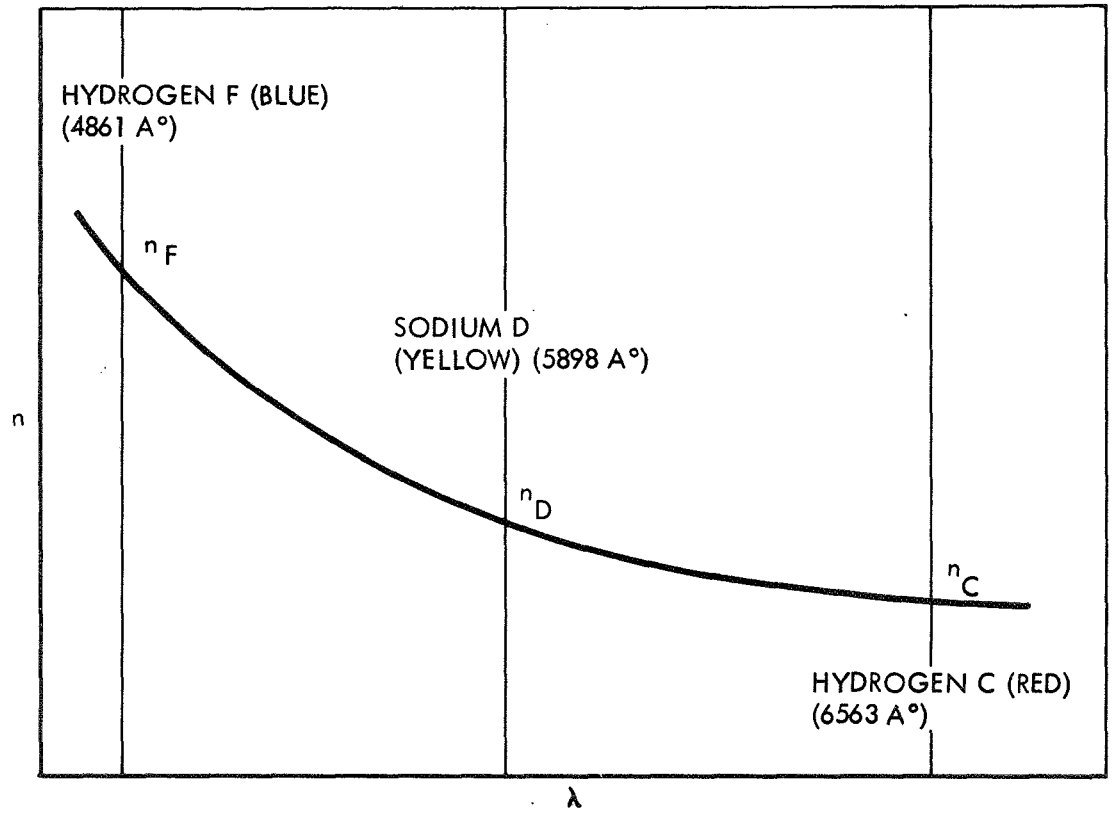


Figure 1. Schematic of a Typical n Vs. λ Curve

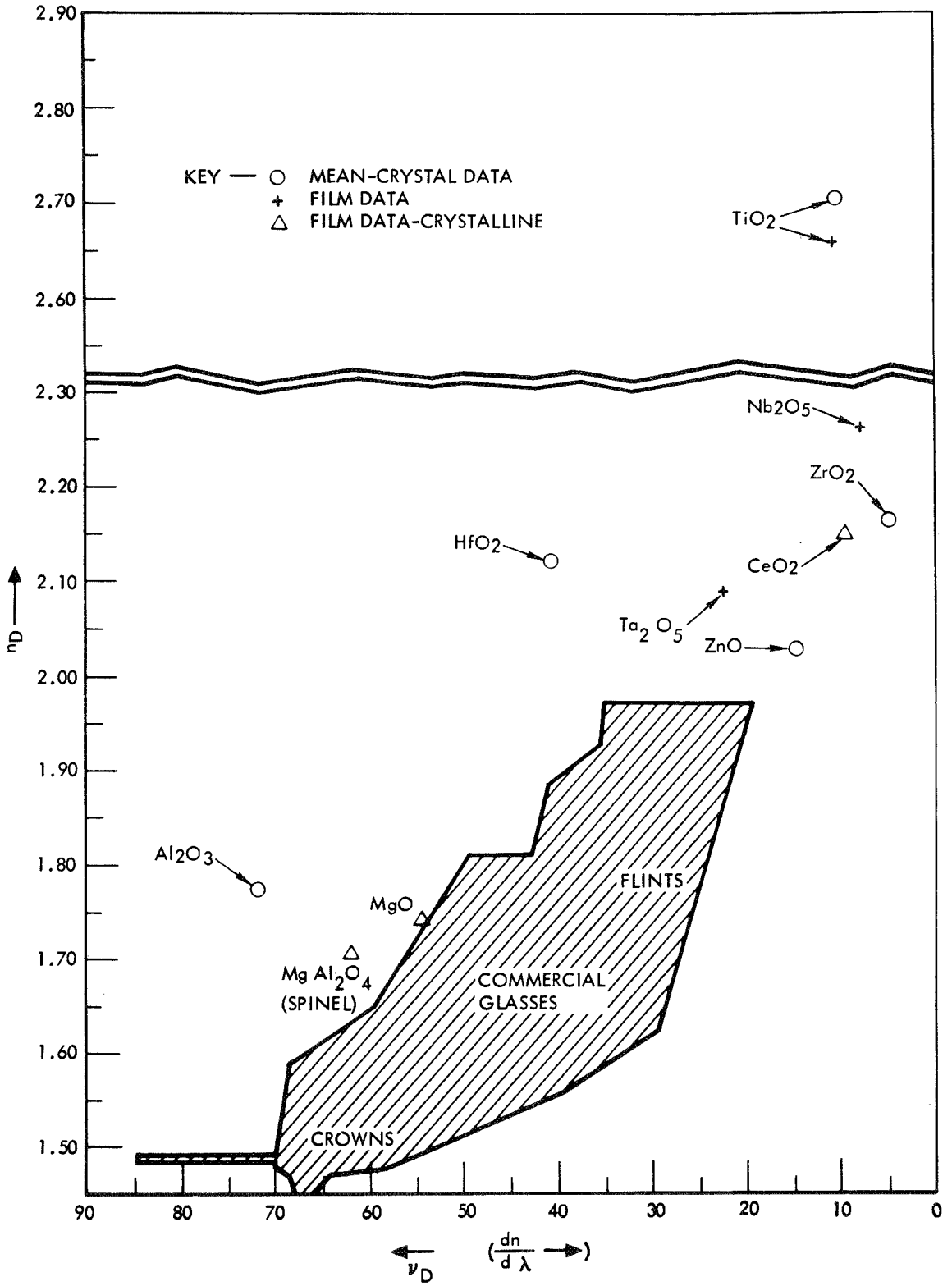


Figure 2. Refractive Index Vs. ABBE Numbers for Oxides

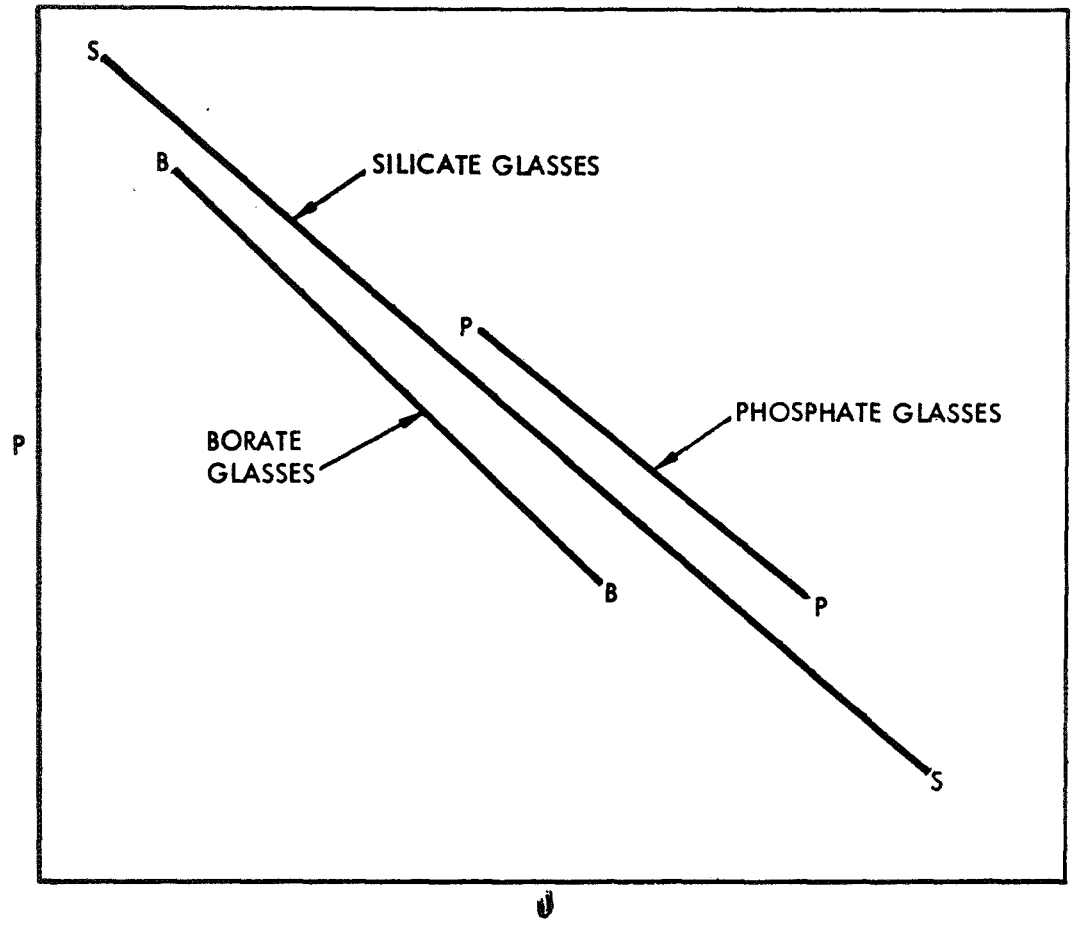


Figure 3. Schematic of a Partial Dispersion Vs. ABBE Number for Borate, Silicate and Phosphate Glasses

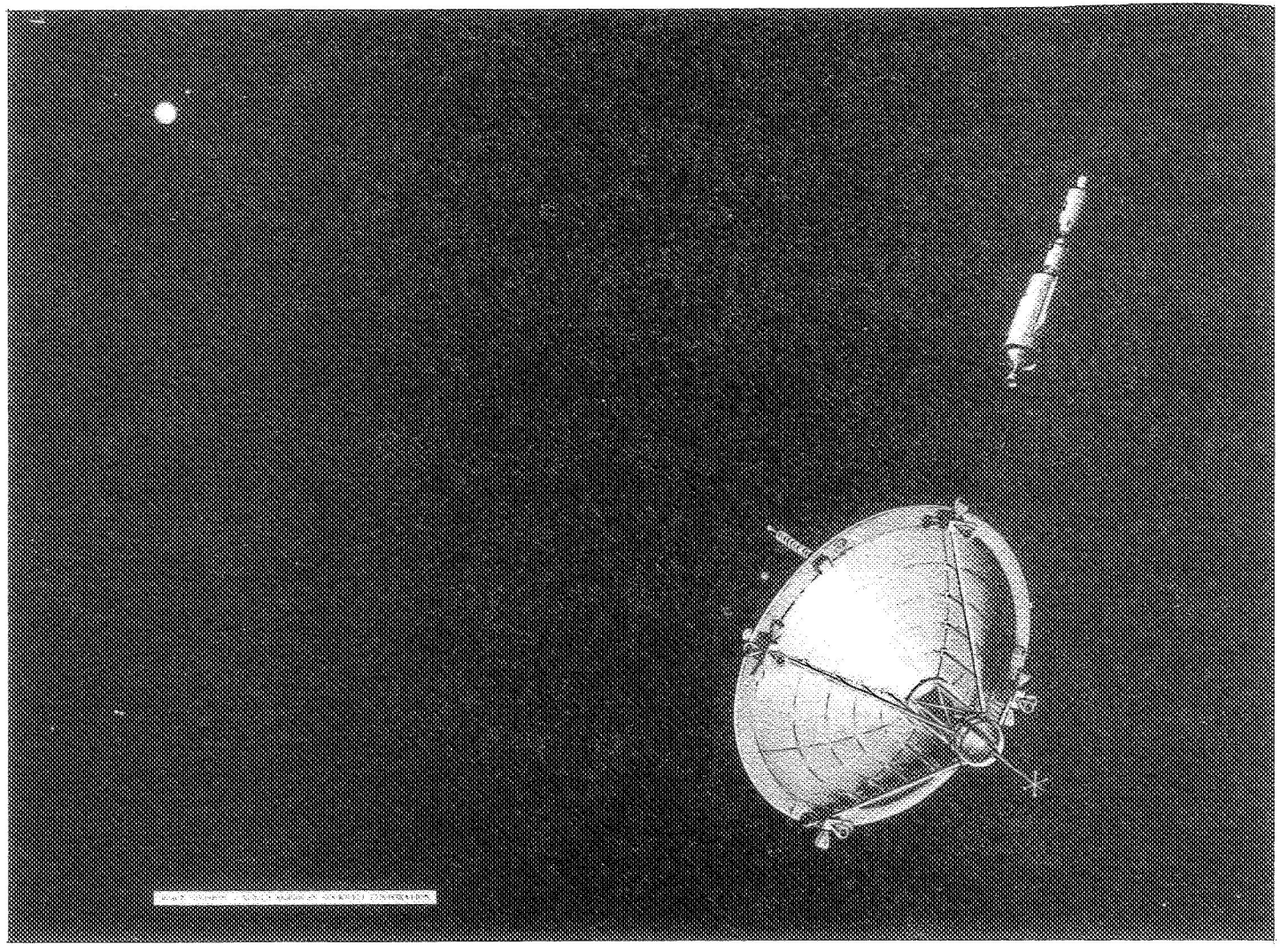


Figure 4. Concept of a Space Solar Furnace

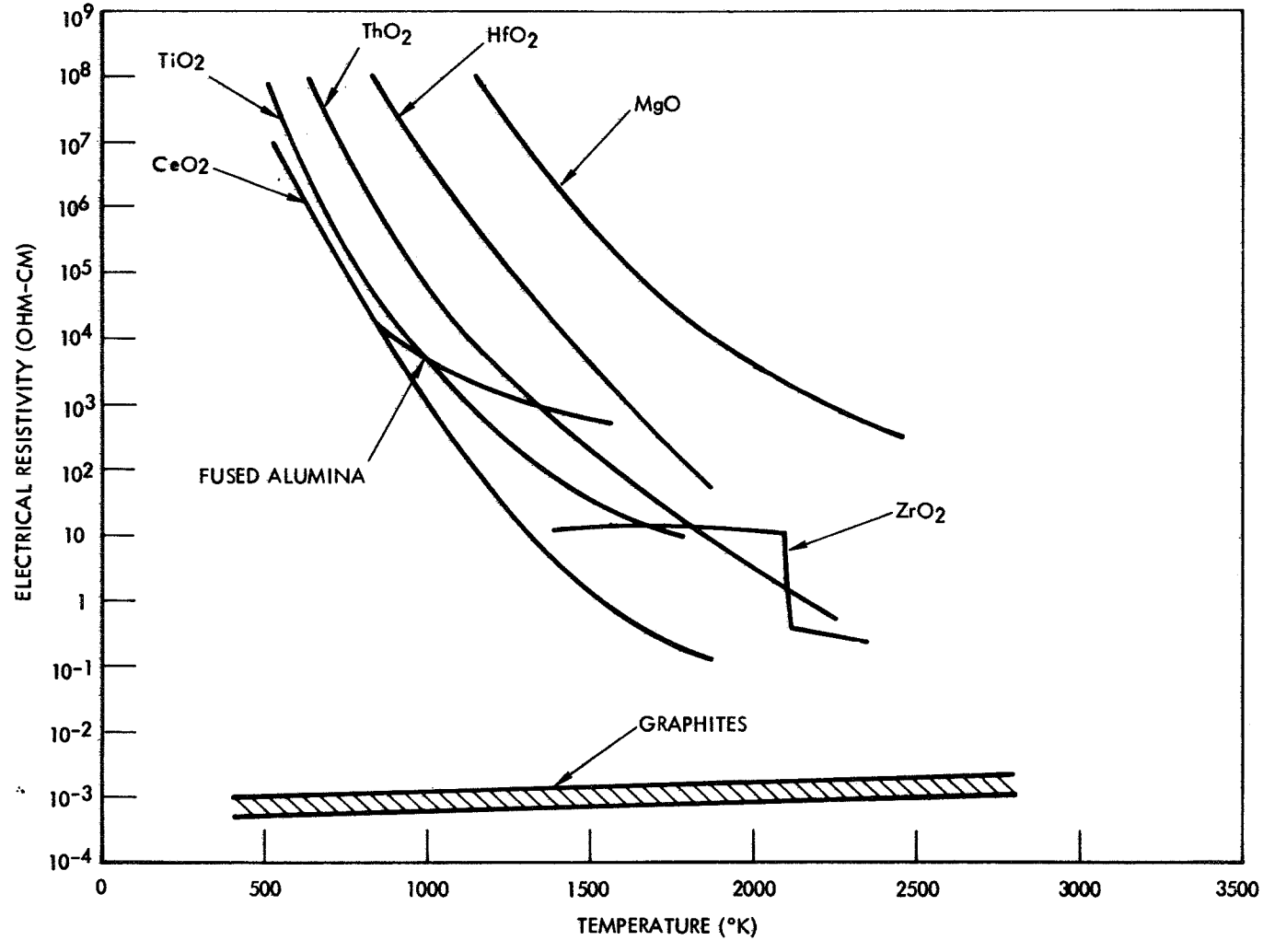


Figure 5. Electrical Resistivity as a Function of Temperature for Some Oxides and Graphite

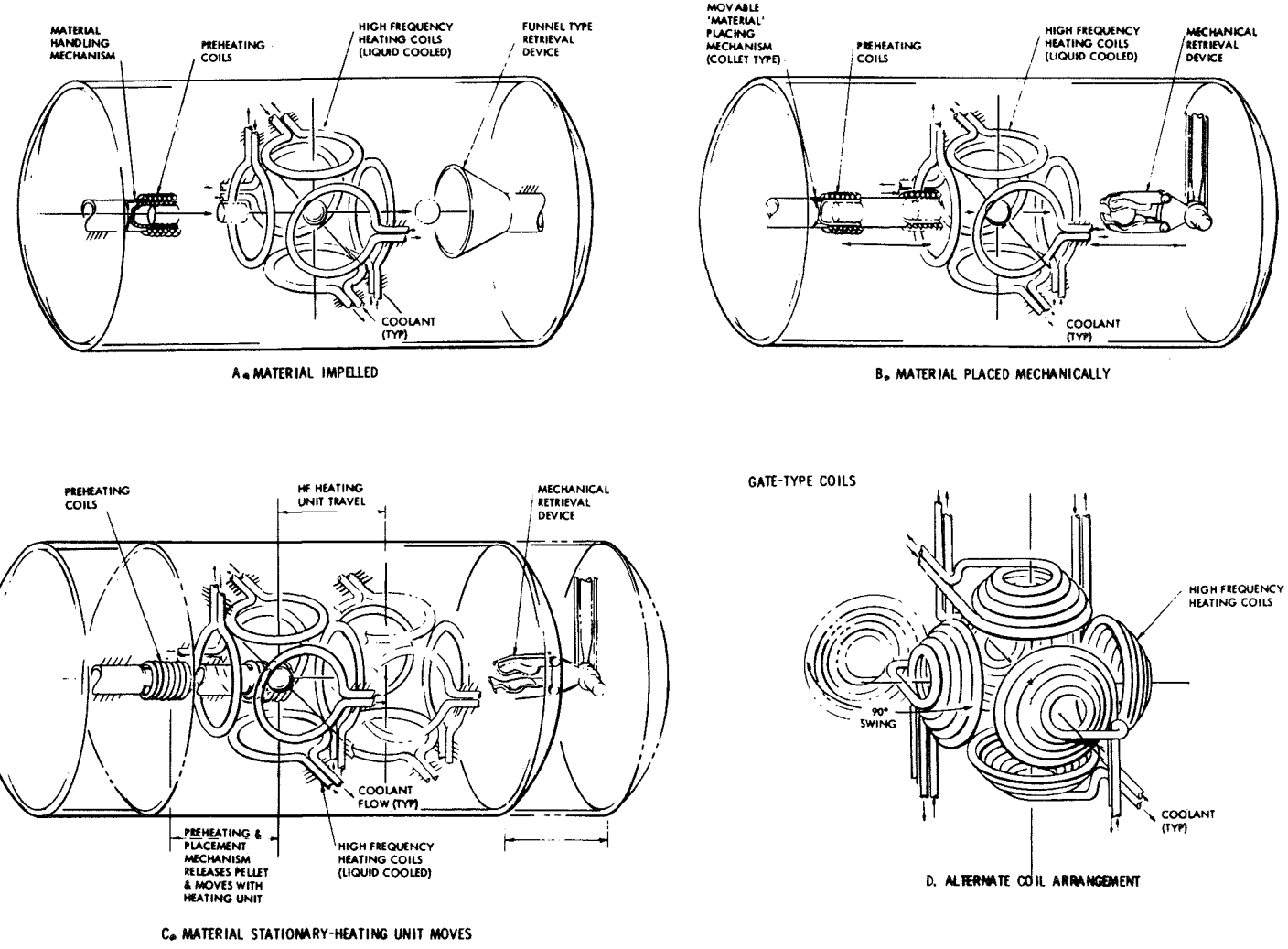
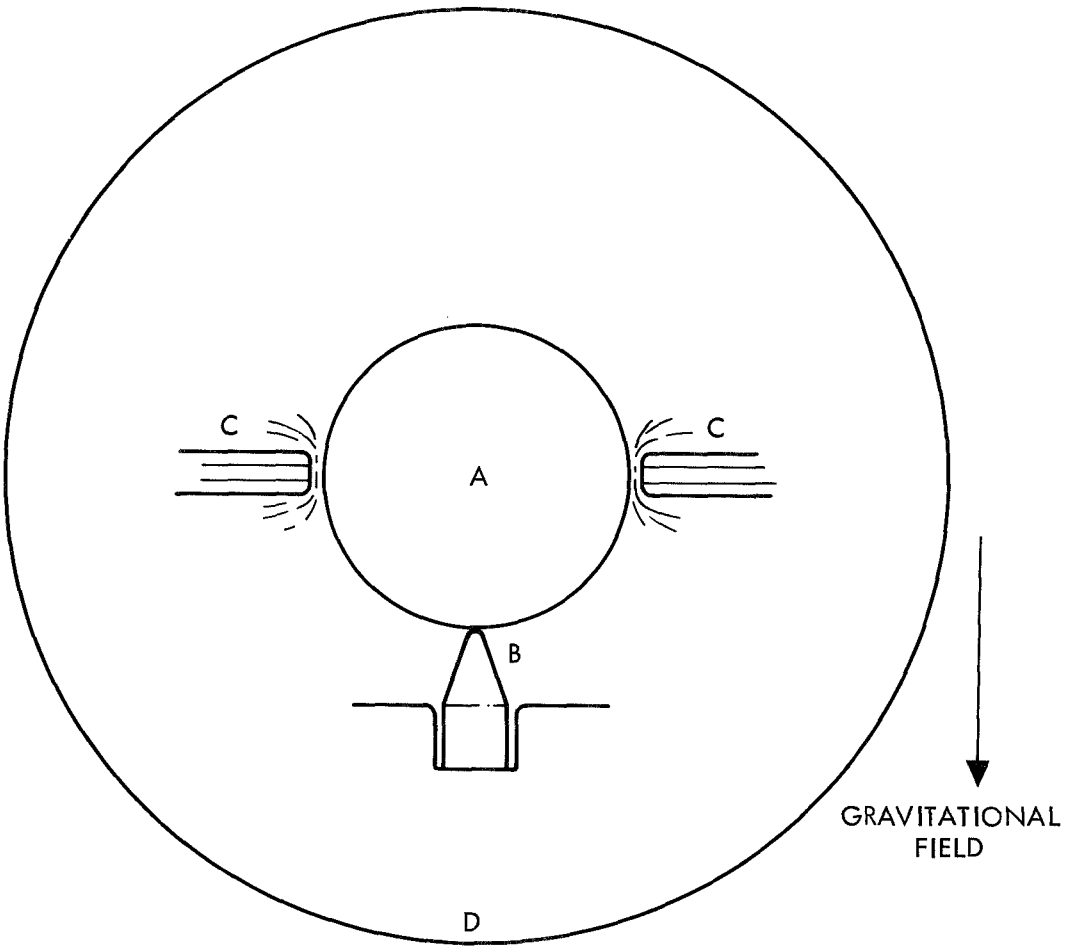


Figure 6. Zero G Induction Melting Concept



A GLASS BODY (SPHERE)

B SEED CRYSTAL

C AIR BEARINGS

D ISOTHERMAL ENCLOSURE

Figure 7. Shcematic of Apparatus for Growing Crystals from Glass